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(21) International Application Number: PCT/US93/09825 (22) International Filing Date: 14 October 1993 (14.10.93) (30) Priority data: 961,966 16 October 1992 (16.10.92) US (71) Applicant: SHELL OIL COMPANY [US/US]; Intellectual Property, P.O. Box 2463, Houston, TX 77252-2463 (US). (72) Inventors: WILPERS, Dale, James ; 18110 Longmoor, Houston, TX 77084 (US). HWO, Charles, Chiu-Hsiung ; 2710 Sugarwood Drive, Sugar Land, TX 77478 (US). LEE, Robert, Wen ; 14827 Bramblewood Drive, Houston, TX 77082 (US). KORCZ, William, Harold ; 3414 Rockyridge, Houston, TX 77063 (US). MOSTERT, Simon ; 206 Valle del Sol, Santa Fe, NM 87501 (US).		(74) Agents: OKORAFOR, James, O. et al.; Shell Oil Company, Intellectual Property, P.O. Box 2463, Houston, TX 77252-2463 (US). (81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FUNCTIONALIZED MODIFIED HIGH MELT FLOW POLYOLEFINS (57) Abstract It is herein provided a polymer composition having and exhibiting improved bonding to incompatible materials comprising functionalized high melt flow polyolefins and unfunctionalized polyolefins. More specifically, these compositions have and exhibit improved adhesion to polar materials, and improved dyeability and printability.		

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DESCRIPTIONFUNCTIONALIZED MODIFIED HIGH MELT FLOW POLYOLEFINSTechnical Field

This invention generally relates to polyolefins. More particularly, this invention relates to high melt flow polyolefins modified by functionalization, which are then blended with unmodified normal melt flow polyolefins to form unique polymers blends. These blends have among other advantages, improved dyeability, printability, and adhesion to polar materials.

10 Background Art

Polyolefins including polypropylene and polybutylene are very well known in the art. Methods of manufacturing and/or processing polyolefins are also known. For example, it is known that due to the rheological incompatibility between soupy polybutylene and regular melt flow polyolefins, the high melt flow polybutylene tends to flow to the outer layer of the molten polymer pool in the extruder. This phenomenon causes the finished parts to be polybutylene rich on the surface. Functionalization of the high melt flow polybutylene is likewise expected to increase the availability of functional groups on the surface of the finished parts.

Functionalization of polymers is known in the art. Functionalization can be accomplished by methods inclusive of electron discharge (Corona discharge) or flaming (oxidization). In multilayer film or sheet structure of two incompatible materials, these methods or a tie layer adhesive is employed to achieve bonding. An undesired drawback of the current practice is that it requires additional equipment, resulting in additional costs. Thus, a simpler and less expensive method of bonding incompatible polymeric materials together or to other materials would be beneficial.

Disclosure of the Invention

It is an object of this invention to provide polymeric compositions having and exhibiting improved bonding to other incompatible polymeric materials, particularly to polar materials.

It is a further object of this invention to provide a simple and economical method of bonding incompatible polymeric materials.

In accordance with this invention, it is now provided a polymer composition comprising functionalized high melt flow polyolefin and unfunctionalized polyolefin.

The inventive composition has and exhibits improved dyeability and printability, and improved adhesion to polar materials. Functionalization is accomplished by reacting with a carboxylic acid anhydride, which can be exemplified by maleic anhydride.

Very broadly speaking, the practice of this invention involves blending modified high melt polyolefins with unmodified polyolefins to form a blend having certain unique characteristics. The term (un)modified as used herein is interchangeable with the term (non)functionalized. The materials useful in the practice of this invention include polyolefins, and suitable functional groups containing compounds. In these modified compounds, the polymers are chemically modified through chemical reaction such as copolymerization or grafting through an extruder or reactor.

All polyolefin polymers which are capable of being blended are suitable in the practice of this invention. The polymers include polyethylene, polybutene-1 (polybutylene), polybutene, polyketones, polyisoprene, and polymethylpentene and their copolymers. Polypropylene and polybutylene homo and copolymers are the preferred polyolefin polymers.

The useful polybutene-1 homo or copolymer can be isotactic, elastomeric, syndiotactic, or it can have any characteristic that is known or expected of polybutene-1. These polybutene-1 polymers have a melt flow measured by ASTM D1238 Condition "L" at 230°C in the range of from about 20 to

1500, with a preferred range of from about 50 to 1000, and a particularly preferred range of from 100 to 750 g/10 min. These polybutene-1 polymers including their methods of preparation, and their properties are known in the art. An
5 exemplary reference containing additional information on polybutylene is U.S. Patent No. 4,960,820 which is herein incorporated by reference.

The particularly preferred polybutene-1 polymer has a melt flow of 490 g/10 min. at 230°C and a molecular weight
10 of 108,000.

The polypropylene used in the present invention is any crystallizable polypropylene. The polypropylene can be prepared by homopolymerizing propylene irrespective of the method used so long as a crystallizable polypropylene is
15 formed. The preferred polypropylenes are the substantially isotactic polypropylenes prepared by the Ziegler/Natta or $MgCl_2$ -supported catalyst polymerization process.

The propylene polymers usable herein can be either propylene homopolymers or copolymers. If propylene
20 copolymers are used, they can be random or block copolymers with the comonomer content preferably 1-30 mole % of either ethylene, butene, or an alpha olefin having from 5 to 8 carbon atoms.

Propylene polymers useful in the invention
25 preferably have a melt flow of less than 30.0, more preferably from about 1.0 to 10.0 g/10 min., as measured by ASTM D-1238, Condition L at 230°C. A particularly suitable propylene, has a melt flow of 2.8 g/10 min. and is available from Shell Chemical Company, of Houston, Texas as PP5A08.

30 The terms suitable functional group(s) containing compounds refers to compounds wherein the functional group is polar. Such components include but are not limited to anhydrides, carboxylates and acrylates. The preferred compound is maleic anhydride.

35 The functionalized polymer of this invention has numerous uses. For example, it is useful in producing articles of manufacture such as films, molded parts such as

cups, trays, and containers, and textiles. The functionalized polymer is expected to show improved adhesion, especially to polar substrates, such as EVOH, EVA, aluminum, polyamides, polyesters, polyacrylates and ionomers.

5 The invention can be further illustrated by the following prophetical example.

Example 1

 An unmodified polypropylene with melt flow of 2.8 can be dry-blended or melt-compounded with modified high melt
10 flow (MF = 490) polybutylene. The blended product can then be made into sheets of 20 mils in thickness either by an extruder coupled with a sheet casting die or a hot platen press. The said sheet can then be stretched using a film
15 stretcher such as the one made by the T.M. Long Company. The stretching can be done simultaneously or sequentially at 4.4 stretch ratio in both machine and transverse directions. The drawing conditions, for example, can be:

 Drawing Temperature - 150°C

 Drawing Speed - 30 mm/sec.

20 Preheat Time - 3 min.

 Grip Force - 125 psi

 The resulting films of about 1 mil in thickness can be compared with materials of the 100% unmodified polypropylene. The film made of unmodified polypropylene plus 5 weight
25 percent high melt modified polybutylene can have better dyeability, printability, and adhesion to polar materials than the film made of 100% unmodified polypropylene.

 While this invention has been described in detail for the purpose of illustration, it is not to be construed as
30 limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

CLAIMS

1. A polymer composition having and exhibiting improved bonding and printability comprising functionalized high melt flow polyolefins and unfunctionalized polyolefins.

2. A polymer composition having and exhibiting improved bonding and printability comprising functionalized high melt flow polybutylene and unfunctionalized polypropylene.

3. A composition as in claim 1 wherein said functionalization is accomplished by means of one or more members selected from the group consisting of anhydrides, carboxylates and acrylates.

4. A composition as in claim 2 wherein said functionalization is accomplished by means of one or more members selected from the group consisting of anhydrides, carboxylates and acrylates.

5. A composition as in claim 3 wherein said group member is maleic anhydride.

6. A composition as in claim 4 wherein said group member is maleic anhydride.

7. A composition as in claim 1 having and exhibiting improved adhesion to polar materials.

8. A composition as in claim 2 having and exhibiting improved adhesion to polar materials.

9. An article of manufacture made from the composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/09825

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L23/02 //(C08L23/02, C08L51:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 886 227 (R. E. VAN BREDERODE) 27 May 1975 Abstract see column 7, line 35 - column 8, line 67 ---	1-9
X	CHEMICAL ABSTRACTS, vol. 68, no. 14, 1 April 1968, Columbus, Ohio, US; abstract no. 60284j, page 5838 ;column 2 ; see abstract & JP,B,42 019 933 (CHISSO CORP) 5 October 1967 ---	1,3,5,7,9
X	US,A,4 064 315 (BIVANS ET AL) 20 December 1977 Abstract see table 1 -----	1,3,5,7,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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